

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
6 May 2004 (06.05.2004)

PCT

(10) International Publication Number
WO 2004/037416 A3

(51) International Patent Classification⁷: **B01J 31/04**,
31/18, 31/22, 31/26, 31/36, C07C 51/145

(21) International Application Number:
PCT/PT2003/000015

(22) International Filing Date: 15 October 2003 (15.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
102859 23 October 2002 (23.10.2002) PT

(71) Applicant (for all designated States except US): IN-
STITUTO SUPERIOR TÉCNICO [PT/PT]; GAL-
TEC/GAPI, Avenida Rovisco Pais, 1049-001 Lisbon (PT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **POMBEIRO**,
Armando, [PT/PT]; IST, Centro de Química Estrutural,
Complexo I, Avenida Rovisco Pais, 1049-001 Lisbon
(PT). **FRAÚSTO DA SILVA**, João [PT/PT]; IST, Centro
de Química Estrutural, Complexo I, Avenida Rovisco
Pais, 1049-001 Lisbon (PT). **FUJIWARA**, Yuzo [JP/JP];
Department of Chemistry and Biochemistry, Graduate
School of Engineering, Kyushu University, Fukuoka,
Fukuoka 812-8581 (JP). **SILVA**, José Armando, [PT/PT];
IST, Centro de Química Estrutural, Complexo I, Avenida
Rovisco Pais, 1049-001 Lisbon (PT). **REIS**, Patrícia M.,
[PT/PT]; IST, Centro de Química Estrutural, Complexo I,
Avenida Rovisco Pais, 1049-001 Lisbon (PT). **PALAVRA**,
António F., [PT/PT]; IST, Centro de Química Estrutural,
Complexo I, Avenida Rovisco Pais, 1049-001 Lisbon (PT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii)) for all designations

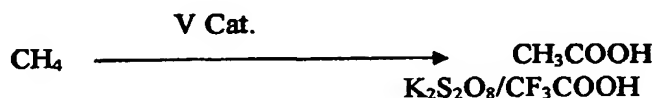
Published:

— with international search report
— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(88) Date of publication of the international search report:
12 August 2004

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: VANADIUM CATALYSTS AND PROCESS FOR THE DIRECT CONVERSION OF METHANE INTO ACETIC ACID



and oxygen (O,O) atoms, namely derivatives of aminoalcohols, (hydroxyimino)dicarboxylic acids, hydroxypyranones, trifluoroacetic acid, triflic acid or inorganic acid, as catalysts for the direct single-pot conversion, under mild conditions, of methane in acetic acid, either in the absence or in the presence of carbon monoxide, and in the presence of a peroxodisulfate salt (K₂S₂O₈), in trifluoroacetic acid (CF₃COOH), according to the general reaction (I).

(57) Abstract: The invention consists on the utilization of complexes of vanadium (in the +4 and +5 oxidation states) with bi- or poly-dentate ligands coordinated by nitrogen and oxygen (N,O) or by oxygen

WO 2004/037416 A3

INTERNATIONAL SEARCH REPORT

national Application No

PT/PT 03/00015

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J31/04 B01J31/18 B01J31/22 B01J31/26 B01J31/36
C07C51/145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | TANIGUCHI Y ET AL: "Highly Efficient Vanadium-Catalyzed Transformation of CH ₄ and CO to Acetic Acid" ORGANIC LETTERS, ACS, WASHINGTON, DC, US vol. 1, no. 4, 8 July 1999 (1999-07-08), pages 557-559, XP002286128 cited in the application the whole document | 1-4 |
| A | NIZOVA G V ET AL: "Carboxylation of methane with CO or CO ₂ in aqueous solution catalysed by vanadium complexes" CHEMICAL COMMUNICATIONS - CHEMCOM, ROYAL SOCIETY OF CHEMISTRY, GB, no. 17, 1998, pages 1885-1886, XP002286129 cited in the application the whole document | 1-3 |
| | --- -/- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the International search

25 June 2004

Date of mailing of the International search report

07/07/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Goebel, M

INTERNATIONAL SEARCH REPORT

national Application No

T/PT 03/00015

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | <p>REIS P M ET AL: "Amavadine as a catalyst for the peroxidative halogenation, hydroxylation and oxygenation of alkanes and benzene"</p> <p>CHEMICAL COMMUNICATIONS - CHEMCOM, ROYAL SOCIETY OF CHEMISTRY, GB , 2000, pages 1845-1846, XP002286130 cited in the application the whole document</p> <p>----</p> | 1-3 |
| A | <p>EP 0 560 656 A (SUMITOMO CHEMICAL CO) 15 September 1993 (1993-09-15) claims; examples</p> <p>----</p> | 1-4 |
| A | <p>ASADULLAH M ET AL: "One-step carboxylation reaction of saturated hydrocarbons with CO by Co(OAc)₂ catalyst under mild conditions"</p> <p>APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 194-195, 13 March 2000 (2000-03-13), pages 443-452, XP004272248 ISSN: 0926-860X the whole document</p> <p>----</p> | 1-4 |
| A | <p>ASADULLAH M ET AL: "CaCl₂-Catalyzed Functionalization of Saturated Hydrocarbons with CO to Carboxylic Acids and Esters"</p> <p>JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 195, no. 1, 1 October 2000 (2000-10-01), pages 180-186, XP004437974 ISSN: 0021-9517 the whole document</p> <p>----</p> | 1-4 |
| A | <p>CRANS D C ET AL: "Vanadium(V)-Protein Model Studies: Solid-State and Solution Structure"</p> <p>JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US , vol. 115, no. 15, 28 July 1993 (1993-07-28), pages 6769-6776, XP002286131 cited in the application page 6769 -page 6770</p> <p>----</p> <p style="text-align: center;">-/--</p> | 3 |

INTERNATIONAL SEARCH REPORT

International Application No
/PT 03/00015

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | <p>BERRY R E ET AL: "The Structural Characterization of Amavadin " ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, WILEY-VCH VERLAG, WEINHEIM, DE , vol. 38, no. 6, 15 March 1999 (1999-03-15), pages 795-797, XP002286132 cited in the application the whole document</p> | 3 |
| A | <p>CARAVAN P ET AL: "Reaction Chemistry of BMOV, Bis(maltolato)oxovanadium(IV)-A Potent Insulin Mimetic Agent" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US , vol. 117, no. 51, 27 December 1995 (1995-12-27), pages 12759-12770, XP002286133 cited in the application page 12759 -page 12760; figures 1,2</p> | 3 |
| A | <p>CHEN C-T ET AL: "Catalytic Nucleophilic Acyl Substitution of Anhydrides by Amphoteric Vanadyl Triflate" ORGANIC LETTERS, ACS, WASHINGTON, DC, US , vol. 3, no. 23, 20 October 2001 (2001-10-20), pages 3729-3732, XP002286134 cited in the application the whole document</p> | 3 |
| A | <p>HAMSTRA B J ET AL: "Structural and Solution Characterization of Mononuclear Vanadium(IV) Complexes That Help To Elucidate the Active Site Structure of the Reduced Vanadium Haloperoxidases" INORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 36, no. 21, 8 October 1997 (1997-10-08), pages 4866-4874, XP002286135 cited in the application page 4866 -page 4867</p> | 3 |

-/--

INTERNATIONAL SEARCH REPORT

national Application No

T/PT 03/00015

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| P,X | <p>REIS P M ET AL: "Single-Pot Conversion of Methane into Acetic Acid in the Absence of CO and with Vanadium Catalysts Such as Amavadin"</p> <p>ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, WILEY-VCH VERLAG, WEINHEIM, DE , vol. 42, no. 7, 17 February 2003 (2003-02-17), pages 821-823, XP002286136</p> <p>the whole document</p> | 1-4 |
| T | <p>CRANS D C ET AL: "The Chemistry and Biochemistry of Vanadium and the Biological Activities Exerted by Vanadium Compounds"</p> <p>CHEMICAL REVIEWS, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 104, no. 2, 29 January 2004 (2004-01-29), pages 849-902, XP002286137</p> <p>page 873</p> | |

INTERNATIONAL SEARCH REPORT
Information on patent family members

national Application No

PT/PT 03/00015

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------------|
| EP 0560656 | A | 15-09-1993 | DE 69310427 D1 12-06-1997 |
| | | | DE 69310427 T2 21-08-1997 |
| | | | EP 0560656 A2 15-09-1993 |
| | | | JP 5345741 A 27-12-1993 |
| | | | US 5281752 A 25-01-1994 |
